FT-Raman, SERS and DFT analysis of safflower red dyed Japanese paper

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Safflower red is a traditional natural dye with a brilliant red hue. It is extracted from the petals of Carthamus tinctorius L. These petals contain a yellow and a red dye. Safflower yellow, also known as hydroxysafflor yellow A (CI Natural Yellow 5), is water soluble and very light fugitive and it was only rarely used as a dye or colorant. The red dye is mainly composed of carthamin (CI Natural Red 26, CI 75140). Despite its poor lightfastness, safflower red was greatly appreciated in Asia as a dye and a colorant for its bright and attractive red color. Safflower was particularly important in *nishiki-e* multicolour Japanese woodblock printing, were it represented the most highly prized red before being supplanted by cochineal in 1869 [1].

In this work, the analysis of washi paper dyed with safflower red was carried out by FT-Raman and SERS spectroscopies. Non-invasive and microanalytical techniques are particularly important for the study of woodblock prints, since the dyes are usually present at very thin layers absorbed by paper fibers. Our goals were to obtain the ordinary Raman spectrum of safflower red, assign its bands, and determine the best experimental conditions for the SERS detection of safflower red in Japanese paper. For this reason, diverse conditions, such as different pH values (neutral and acid), and previous hydrolysis of the dye with HF were studied. In order to get a better knowledge of the effect of the pH in safflower, a SERS study of safflower extract was also carried out.

The FT-Raman spectrum of safflower red was carried out after ethanol extraction from the paper. SERS spectra were obtained from both the alcoholic extract and directly on the dyed paper. Thus, small pieces of fibres were taken from the edges of the paper. A drop of Ag nanoparticles was put on one fibre together with the aggregating agent (KNO_3 or HNO_3). The SERS analysis were collected at 488 nm before drying of the Ag colloid. DFT calculations were also carried out in order to assign the experimental SERS bands to the vibrational normal modes of the dye. The B3LYP/6-31G** was employed to calculate the geometry of safflower red and the Raman spectrum, by means of the Gaussian Software [2].

The FT-Raman spectrum of safflower red shows bands at 1623, 1602, 1586, 1457, 1441, 1297, 1208 and 1172 cm^{-1}. The SERS spectra of the safflower extract on Ag nanoparticles aggregated with KNO_3 (neutral pH) and KNO_3/HNO_3 (acid pH) show several shifts and changes in the relative intensities of the bands. These changes suggest a deprotonation of one of the OH groups of safflower, which leads to an electronic delocalization on the dye molecule. The SERS spectra of the dyed paper with and without HF pre-treatment show similar Raman enhancement (figure 1). However, the SERS spectra after the addition of HNO_3 (figure 1) shows a much lower intensity. Thus, it can be concluded that the best experimental condition for the detection of safflower on paper is the aggregation with KNO_3. The main bands observed in the SERS spectrum are located at 1623, 1603, 1579, 1489, 1423, 1401, 1295, 1244, 1163, 955 and 776 cm^{-1}.

The Raman spectrum obtained from the DFT calculations fits well the experimental spectra. The visualization of the vibrations leads to the assignment of the observed Raman bands to the vibrational normal modes of the red dye. The interaction mechanism of the safflower molecule on the Ag can be concluded from the differences observed between the FT-Raman and SERS spectra of the safflower extract. Several bands are enhanced due to the presence of Ag NPs, such as those observed at 1623, 1583, 1406, 1164, 958, 865, 776, 746 and 733 cm^{-1}.

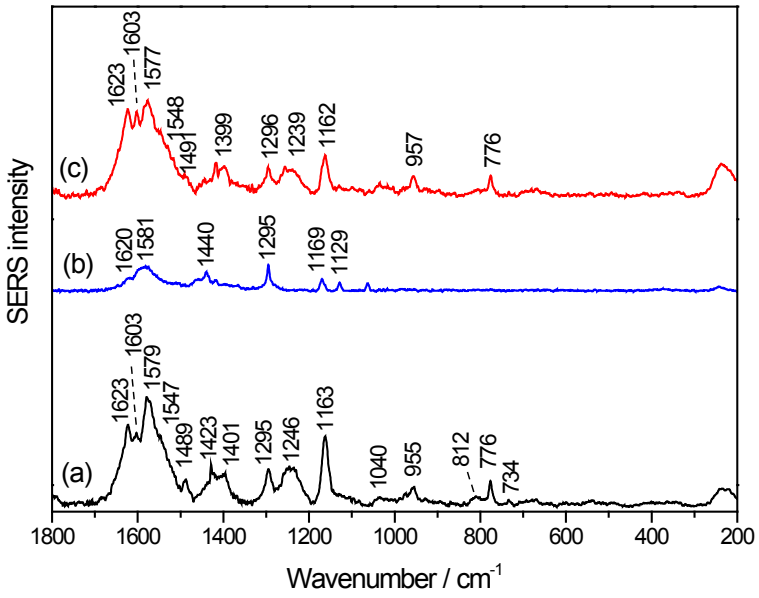

Figure 1. SERS spectra of washi paper dyed with safflower red dye on Ag nanoparticles in different experimental conditions: a) neutral pH: b) acidic pH, and c) after hydrolisis with HF. All the spectra were baseline corrected.

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